

Resilient Sealing Materials for Solid Oxide Fuel Cells

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Outline

Goal: Develop stable, resilient sealing materials for SOFCs

- Reviewing the problem; initial glass development research
- Progress over the past year
 - Glasses with greater CTE's
 - Developing composite materials
- Summarizing our program

The sealing problem is a challenge

1. Challenging compositional design problem

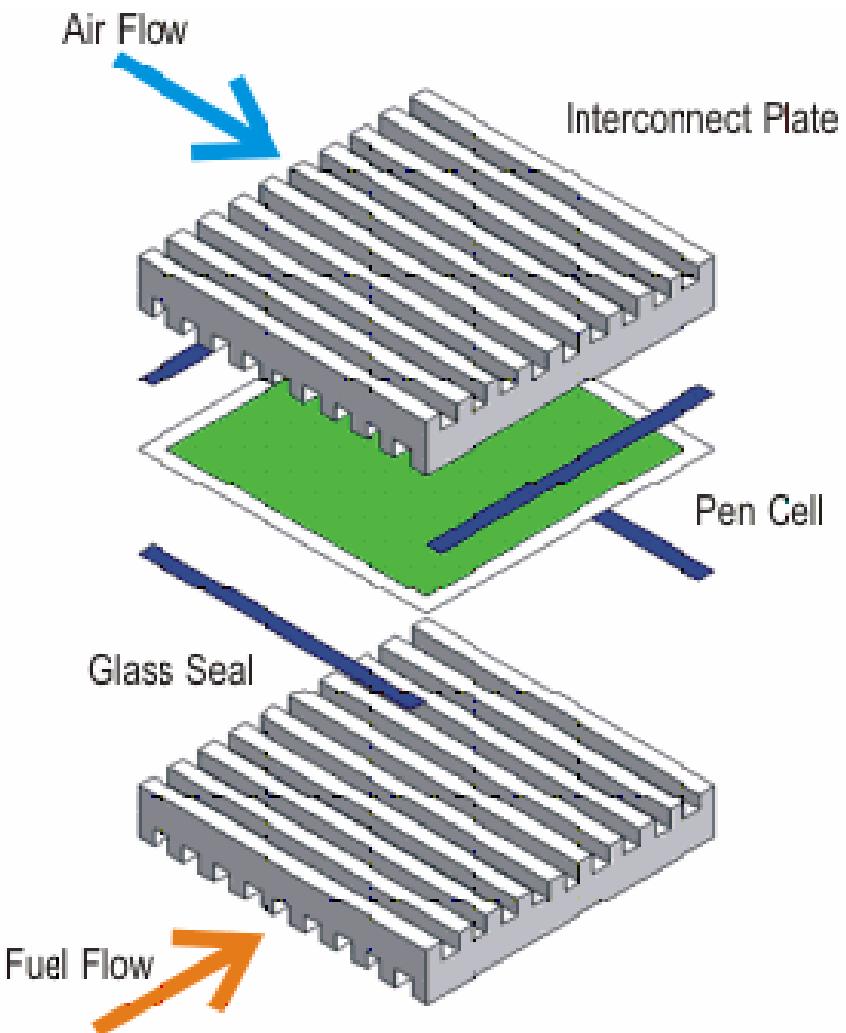
- Uncommon combination of properties
- Investigate uncommon families of glasses

2. Glass-ceramics are a likely option

- Crystallization studies- seal processing and long-term material stability

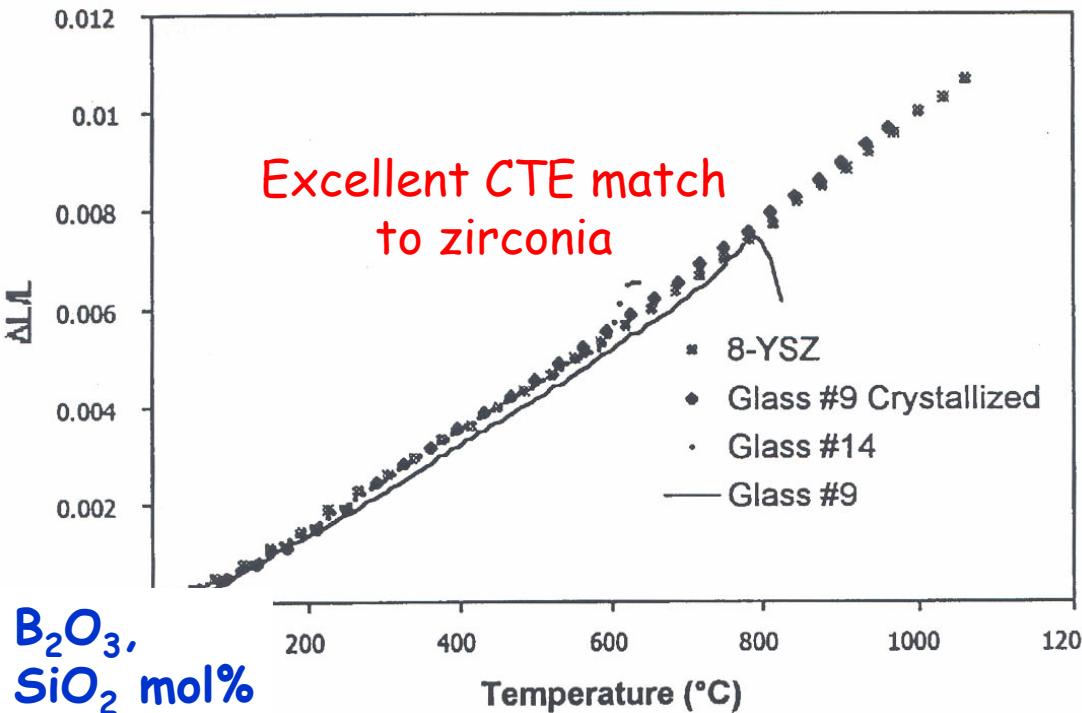
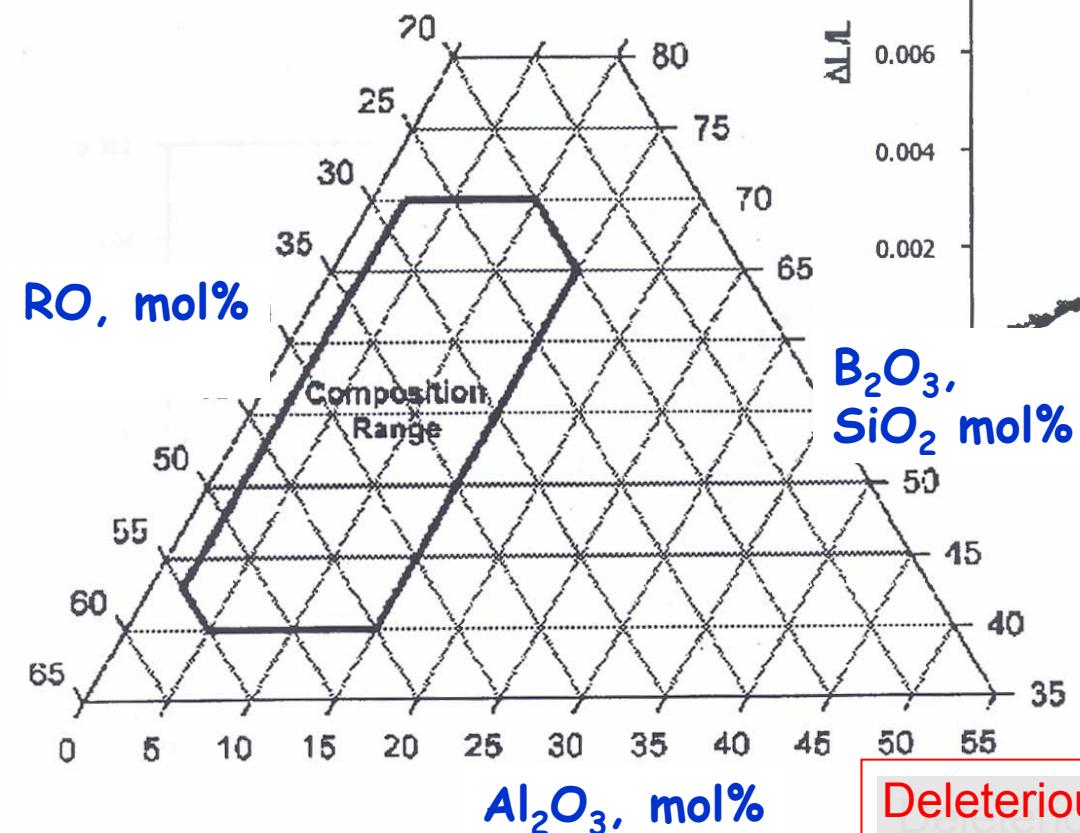
3. Interfacial chemistry

- Glass-metal reactions
- Material stability/volatility
 - Thermochemical stability



Ba-silicate glass-ceramics have shown promise

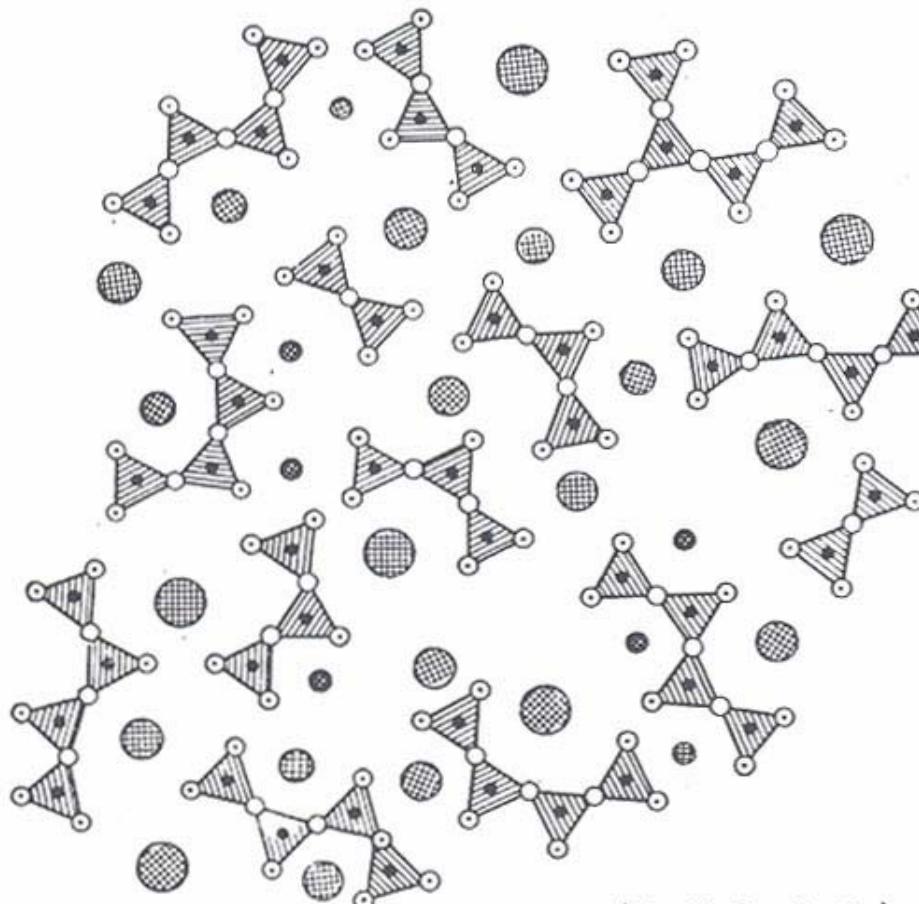
Meinhardt, et al., USP 6,532,769
Mar. 18, 2003



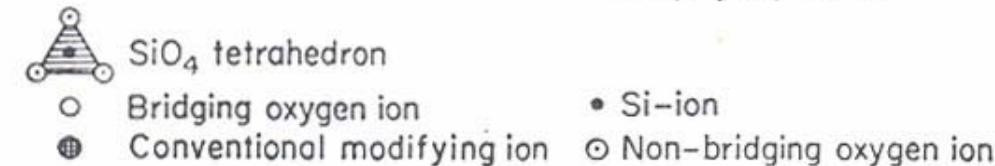
Sealed, crystallized to form high CTE Ba-silicate & Ba-alumino-silicate phases; e.g., $\text{BaO}\cdot 2\text{SiO}_2$, $2\text{BaO}\cdot 3\text{SiO}_2$

Deleterious interfacial reactions: Ba-chromates

Promising glasses have unusual structures



(Na, K, Ca, Sr, Ba)



"Invert Glasses": discontinuous silicate anions tied-together through modifying cations.

- Greater CTE's
- More fragile viscosity behavior
 - 'shorter' glasses
- More 'basic' reaction chemistries

- Metasilicates (chains): $[\text{O}]/[\text{Si}] \sim 3.0$
- Polysilicates (short chains):
 $[\text{O}]/[\text{Si}] > 3.0$

UMR glass-ceramics under development

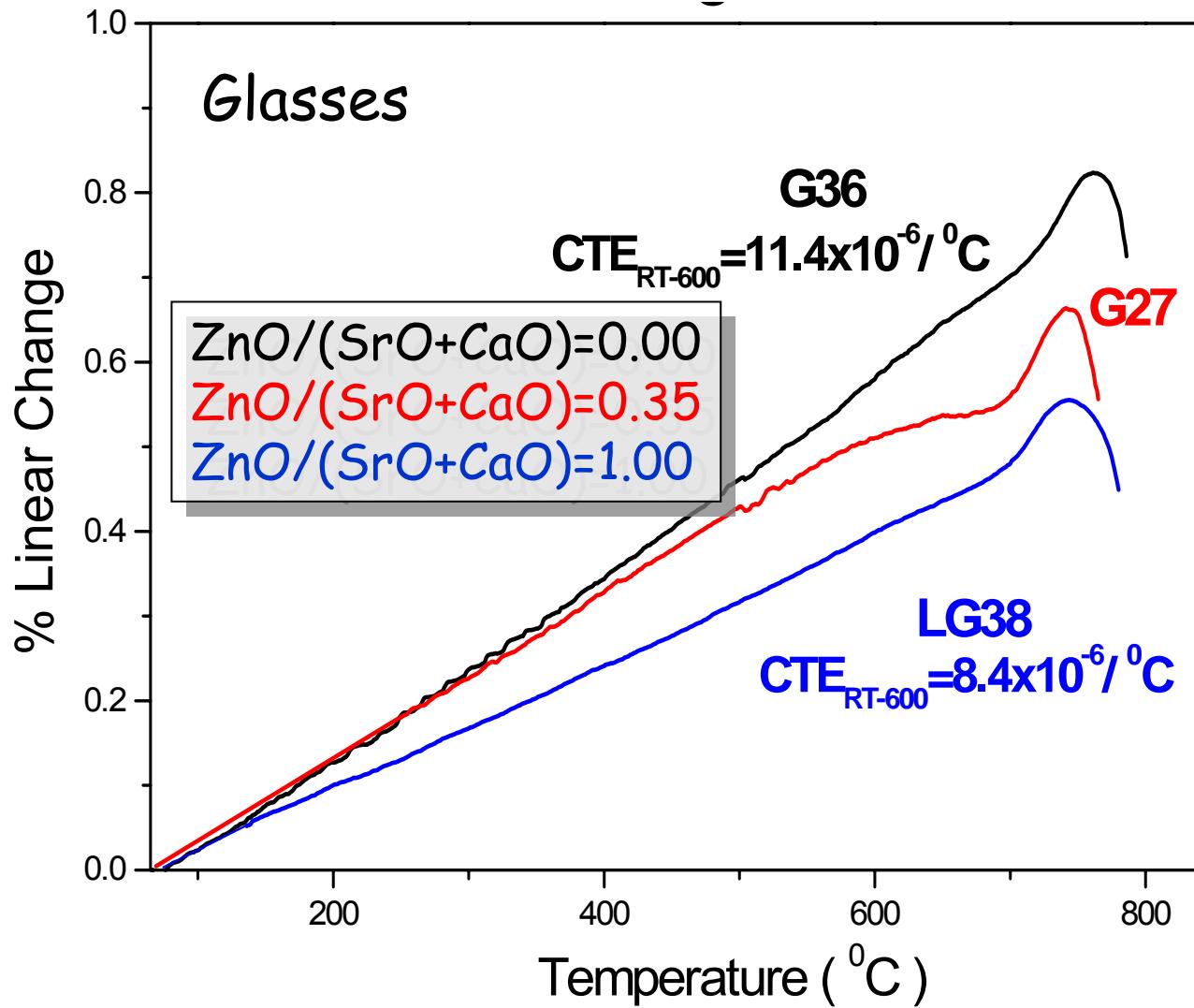
ZnO-modified alkaline earth invert silicates

- Mixed CaO, SrO, ZnO (45-55 mole%)
 - BaO-free
- $[O]/[Si] > 3.3$, $SiO_2 < 45$ mole%
- Minor oxides include Al_2O_3 , B_2O_3 , TiO_2

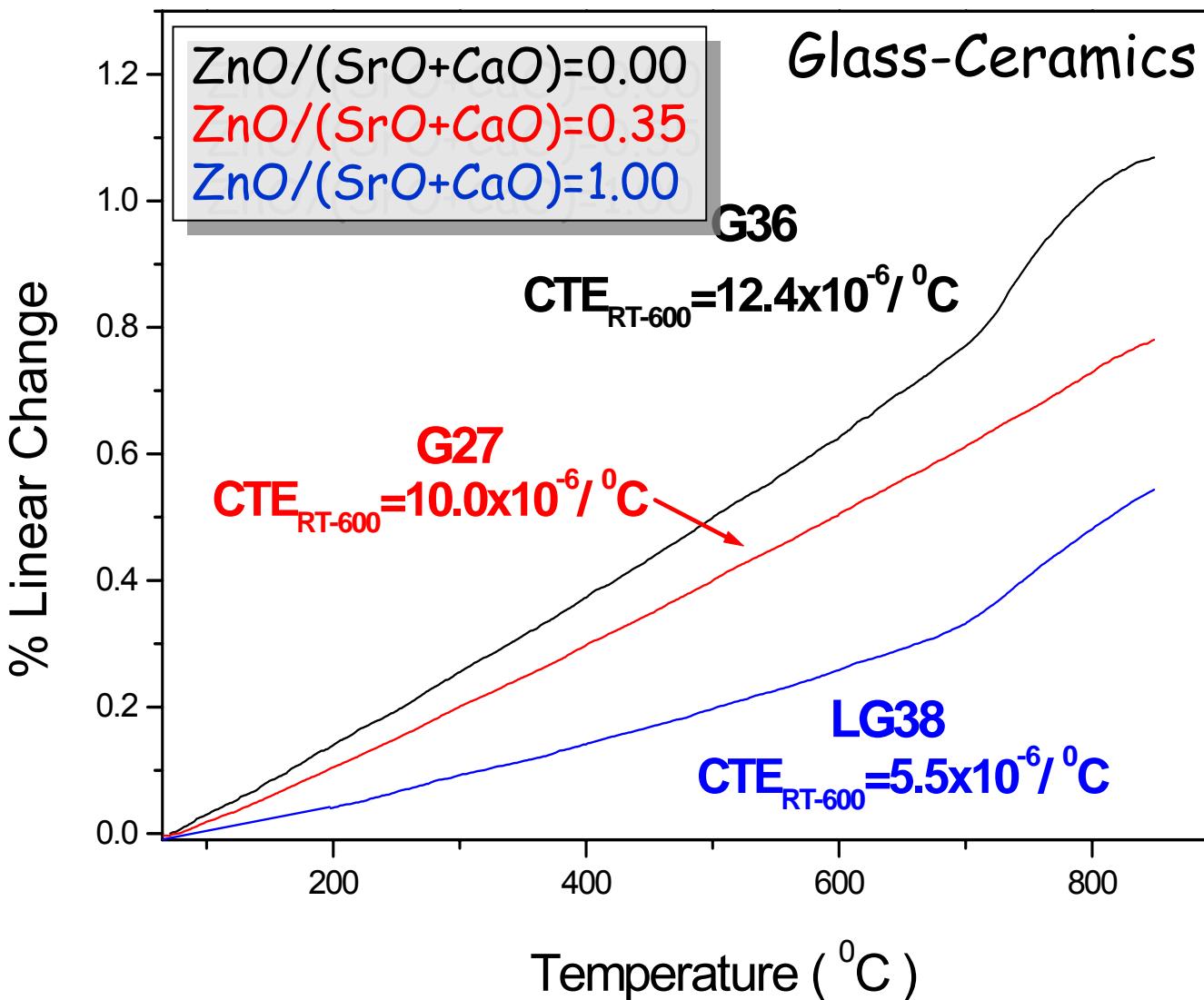
Property design targets:

- Seal/crystallized $< 900^\circ C$
- CTE-match to SOFC components
 - Thermomechanically stable at $> 750^\circ C$
- Thermochemically stable in oxidizing/reducing conditions

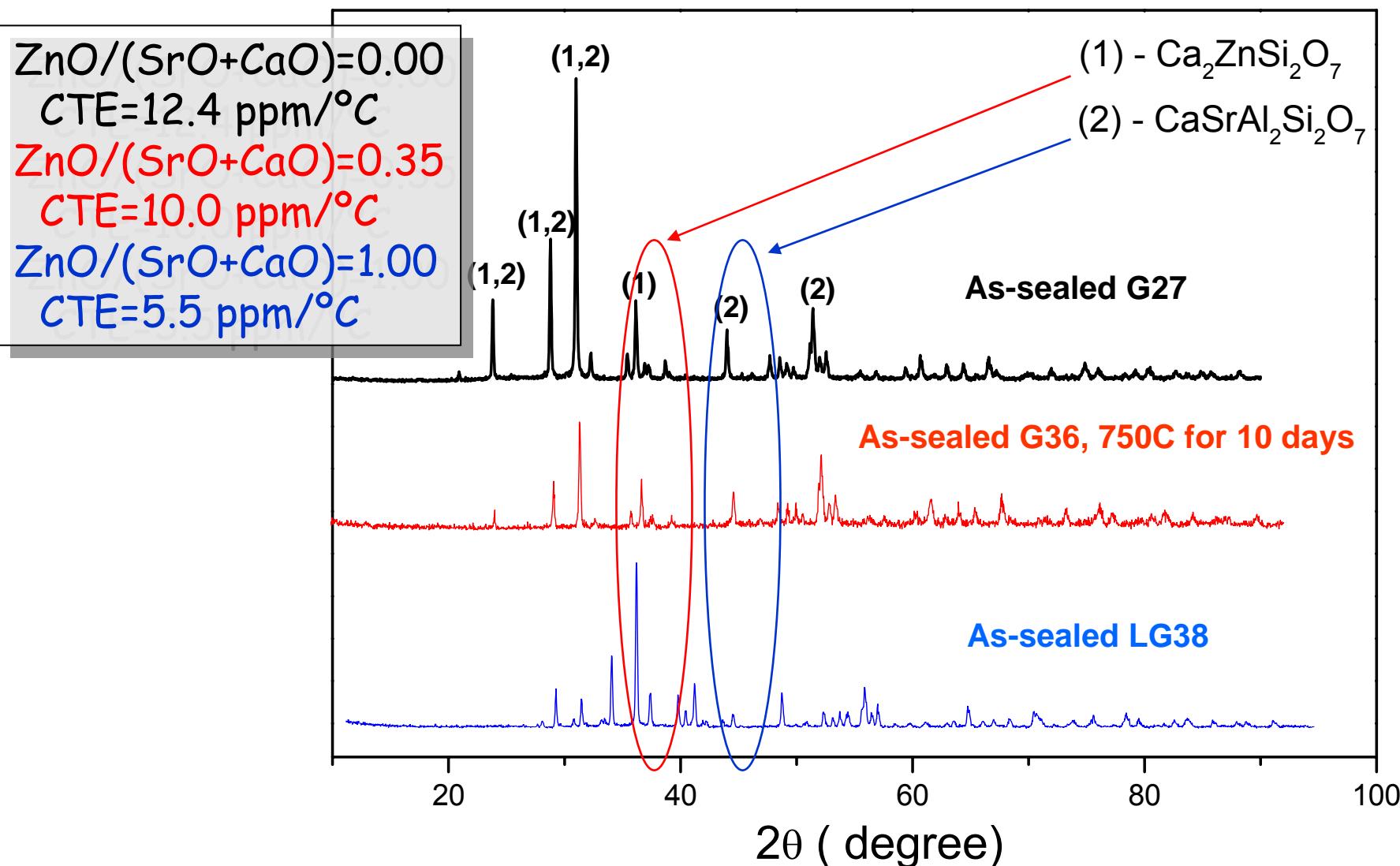
Sealing glass properties depend on composition



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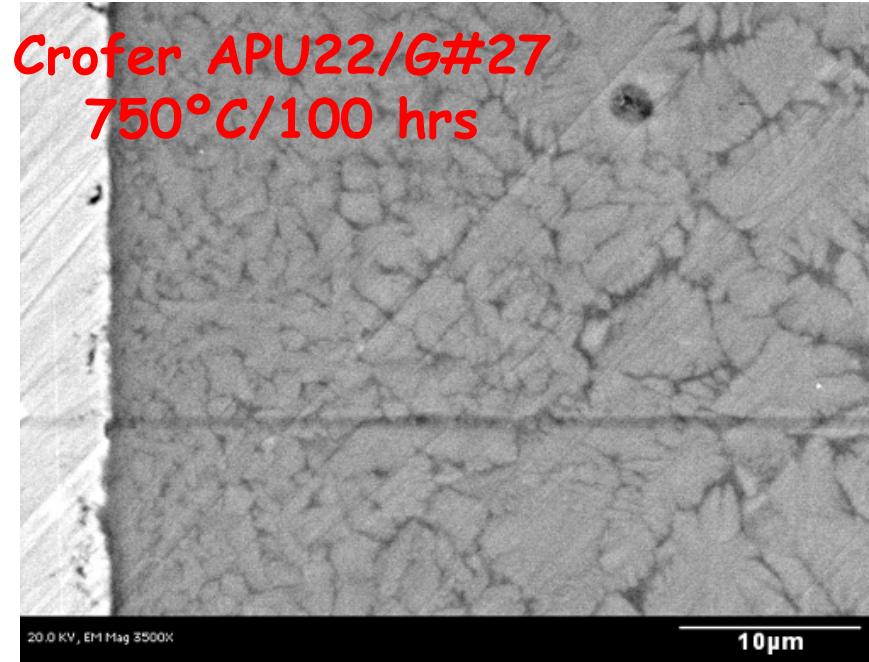


Thermal properties of sealing glasses are controlled by the ZnO/RO ratio

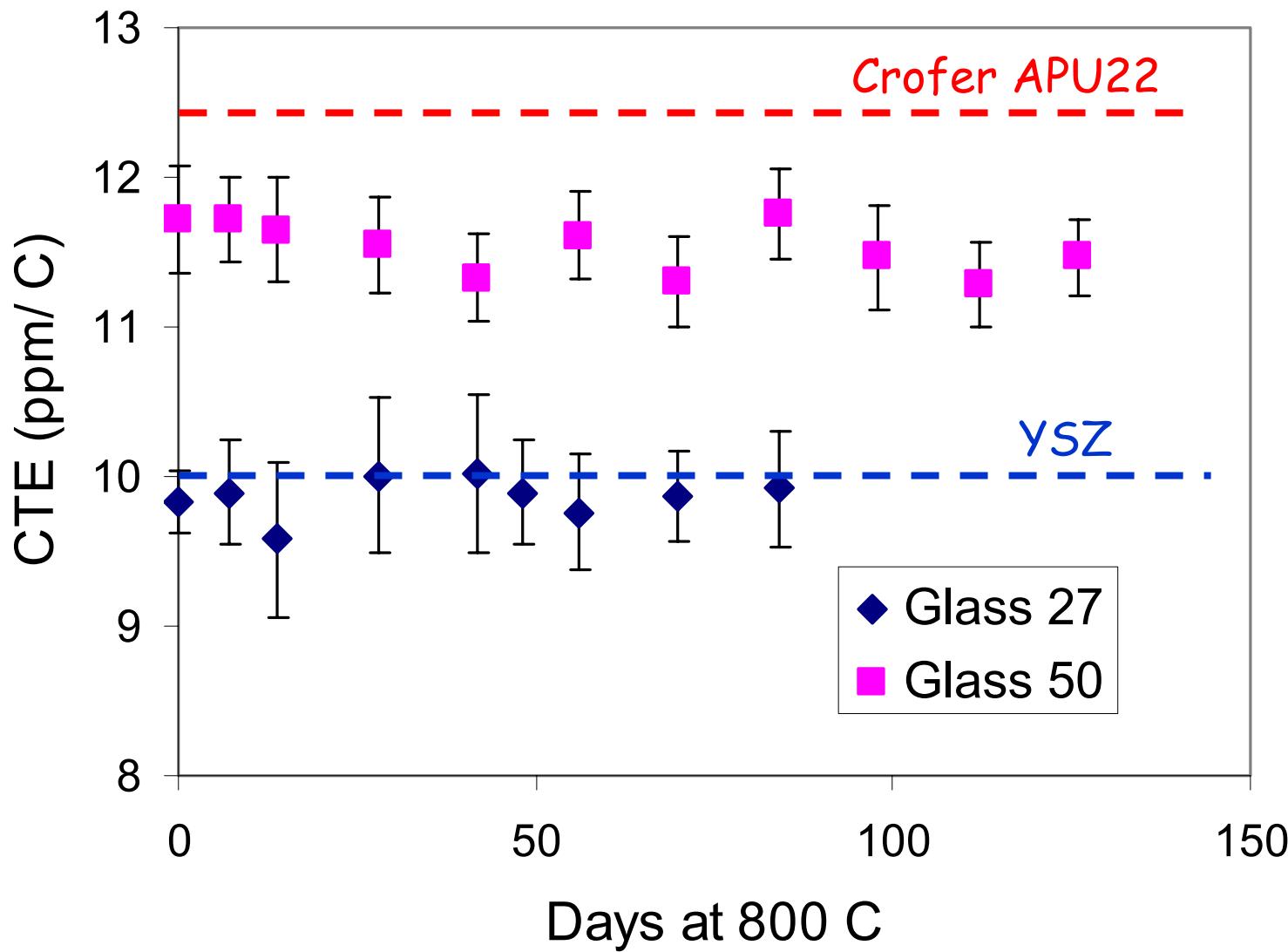


Representative crystalline phases in the UMR glass-ceramics

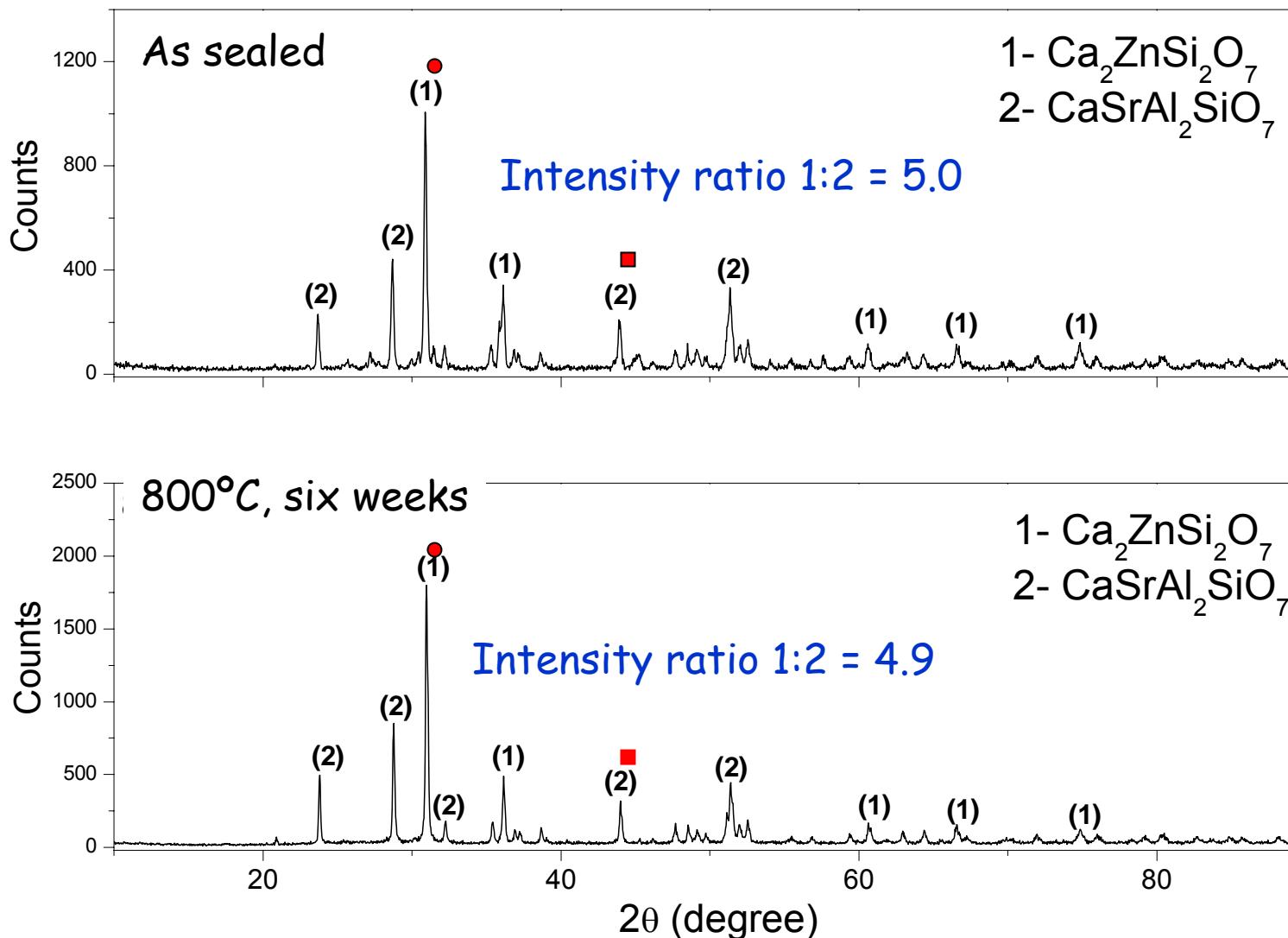
- Pyrosilicates
 - $\text{CaSrAl}_2\text{SiO}_7$,
 $\text{Ca}_2\text{ZnSi}_2\text{O}_7$
- Orthosilicates
 - Sr_2SiO_4 , Zn_2SiO_4
- Composition is most important parameter for final phase distribution.



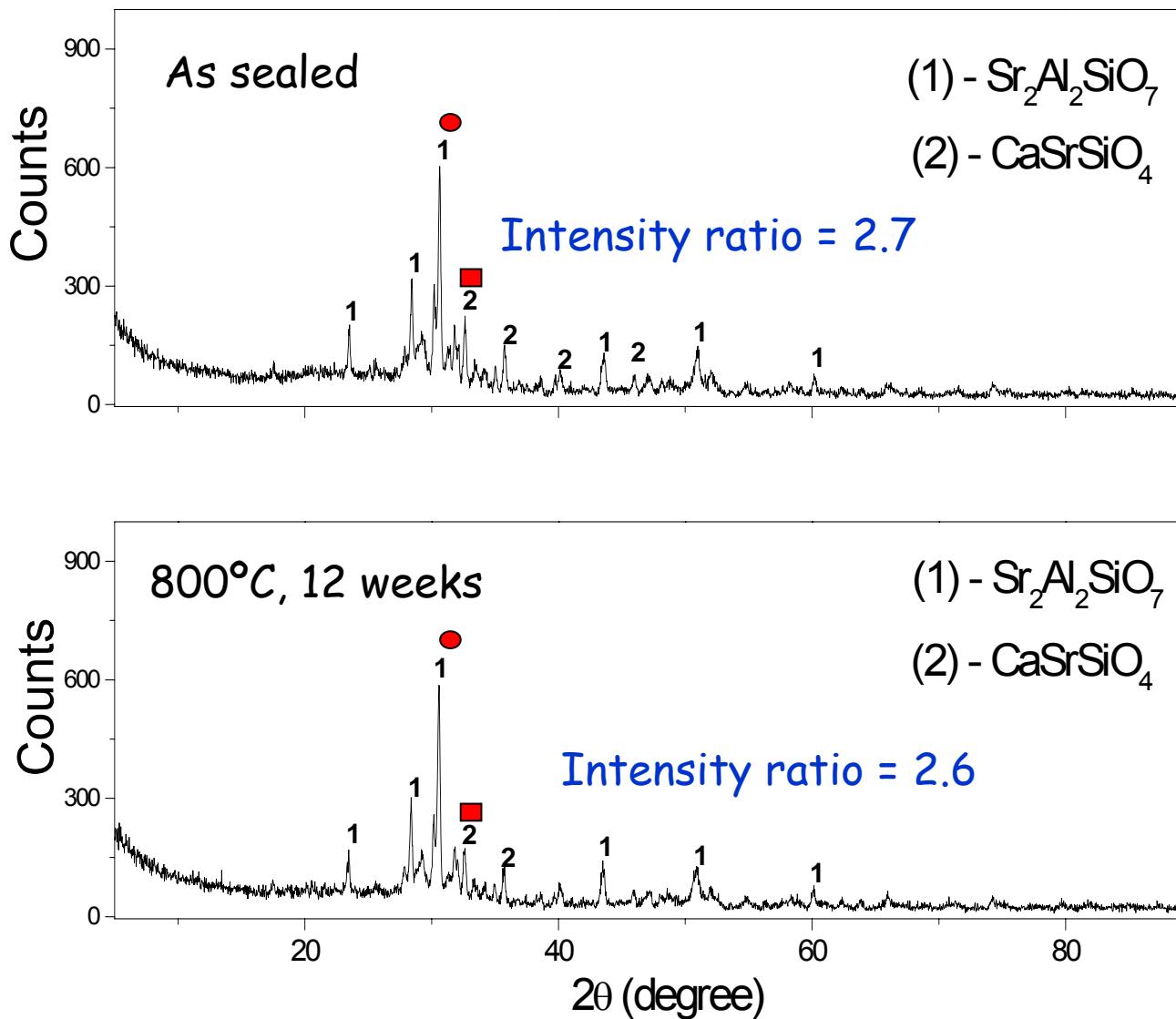
Certain compositions possess good thermal stability



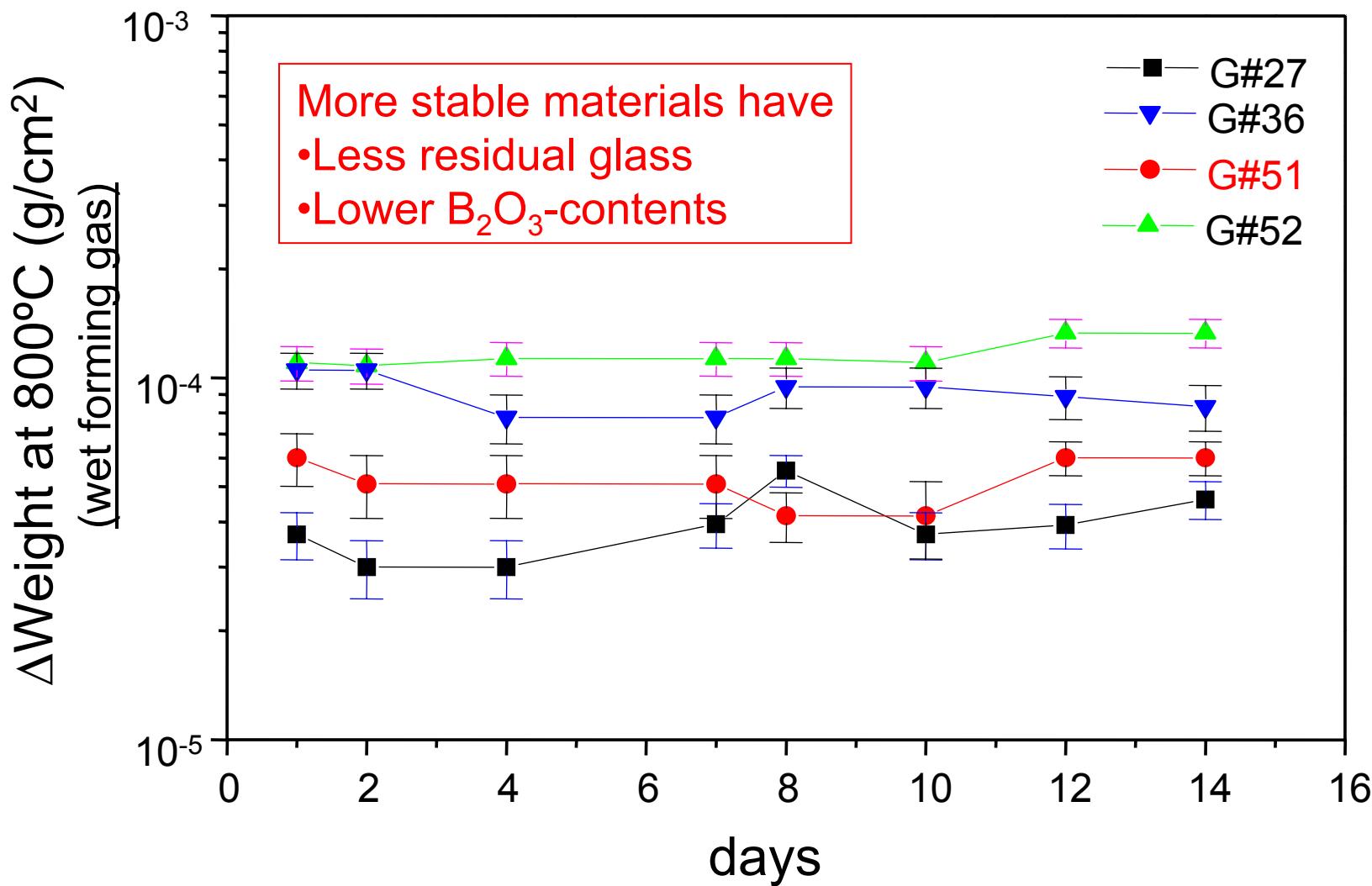
XRD reveals no significant changes in Glass 27 phase distributions



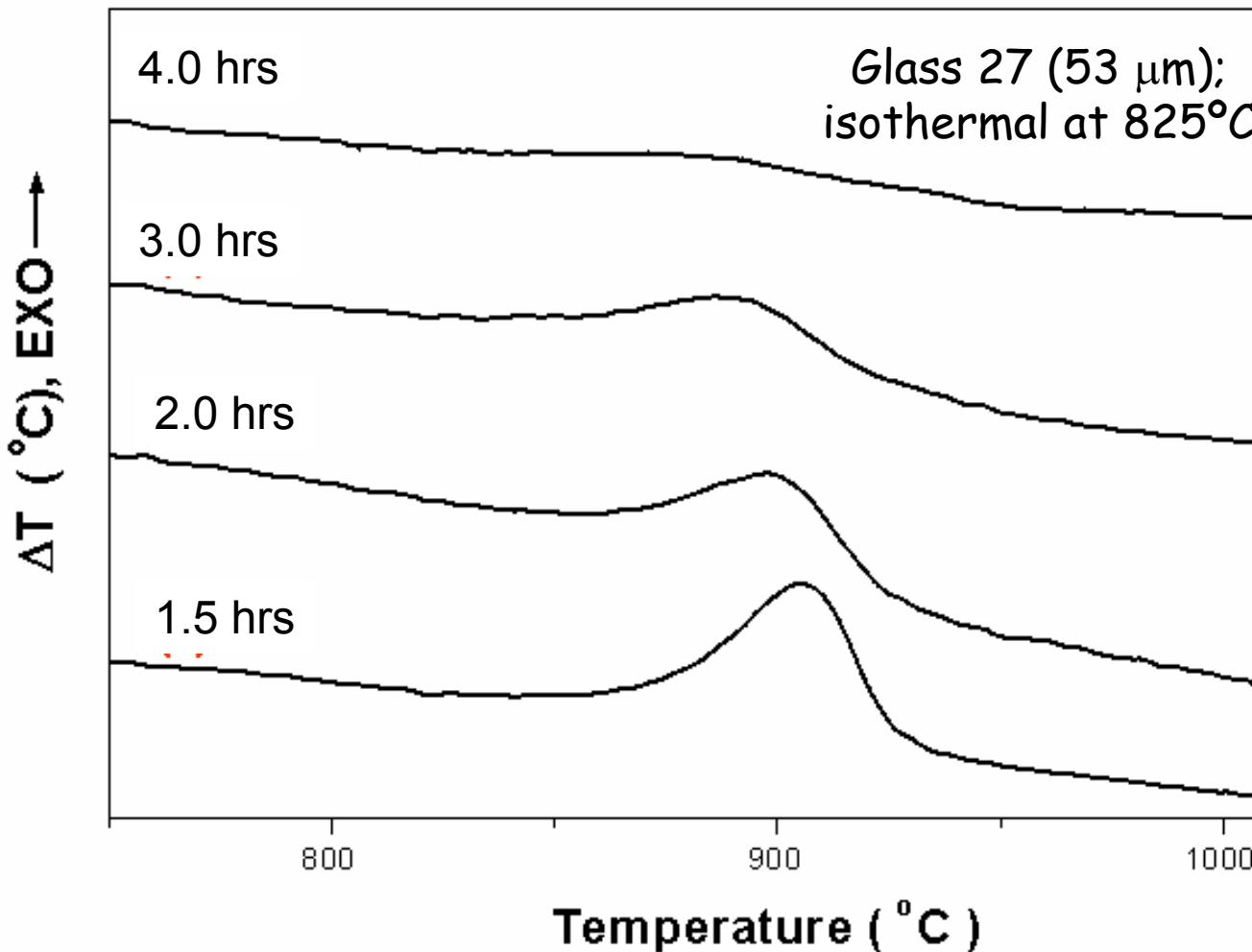
XRD reveals no significant changes in Glass 50 phase distributions



Low-boron glasses are more stable in wet forming gas (800°C)

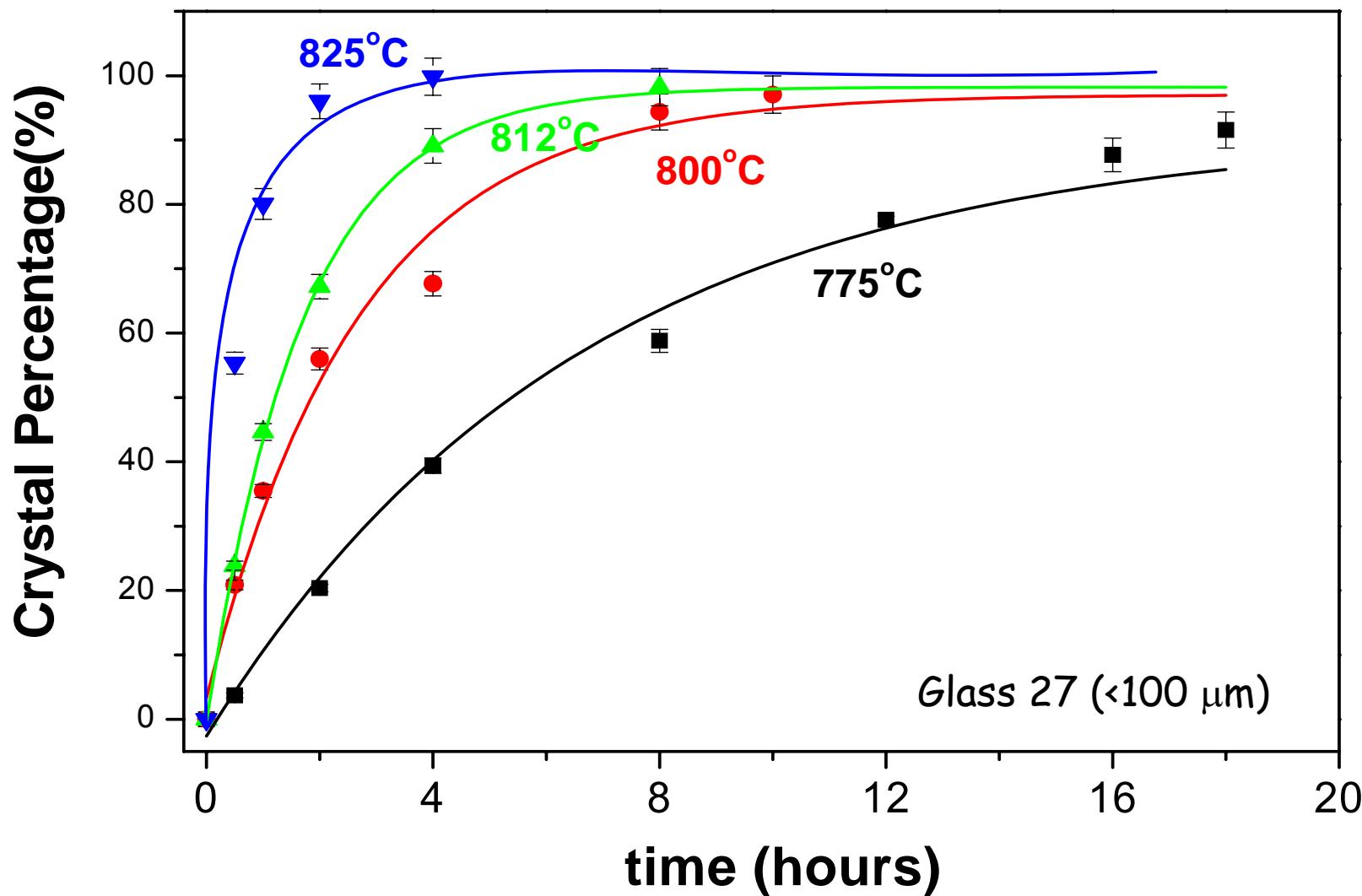


We use DTA to characterize crystallization kinetics



Longer heat treatments leave less residual glass to crystallize on reheating

DTA provides quantitative crystallization information

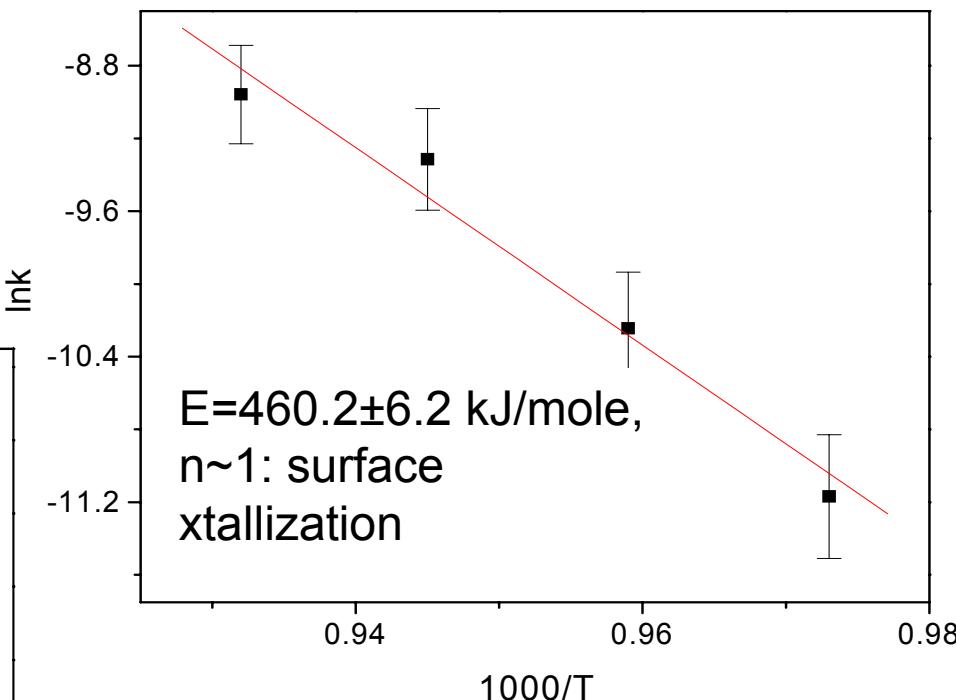
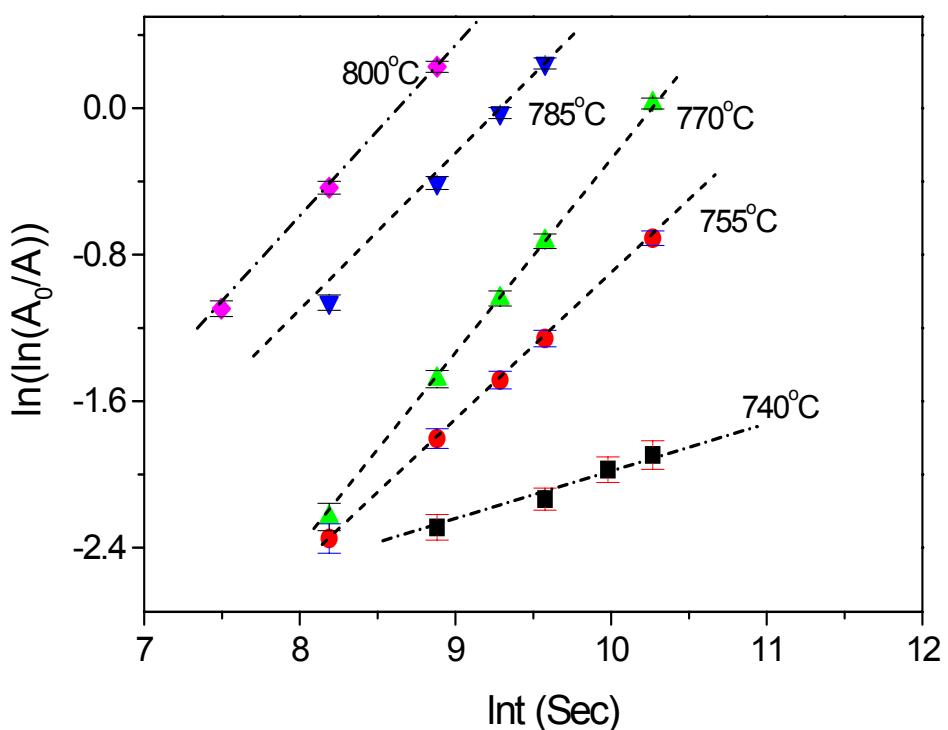


DTA provides quantitative crystallization kinetics

JMA (Avrami) crystallization kinetics:

$$x = 1 - \exp[-(kt)^n], k = k_0 \exp[-E/RT]$$

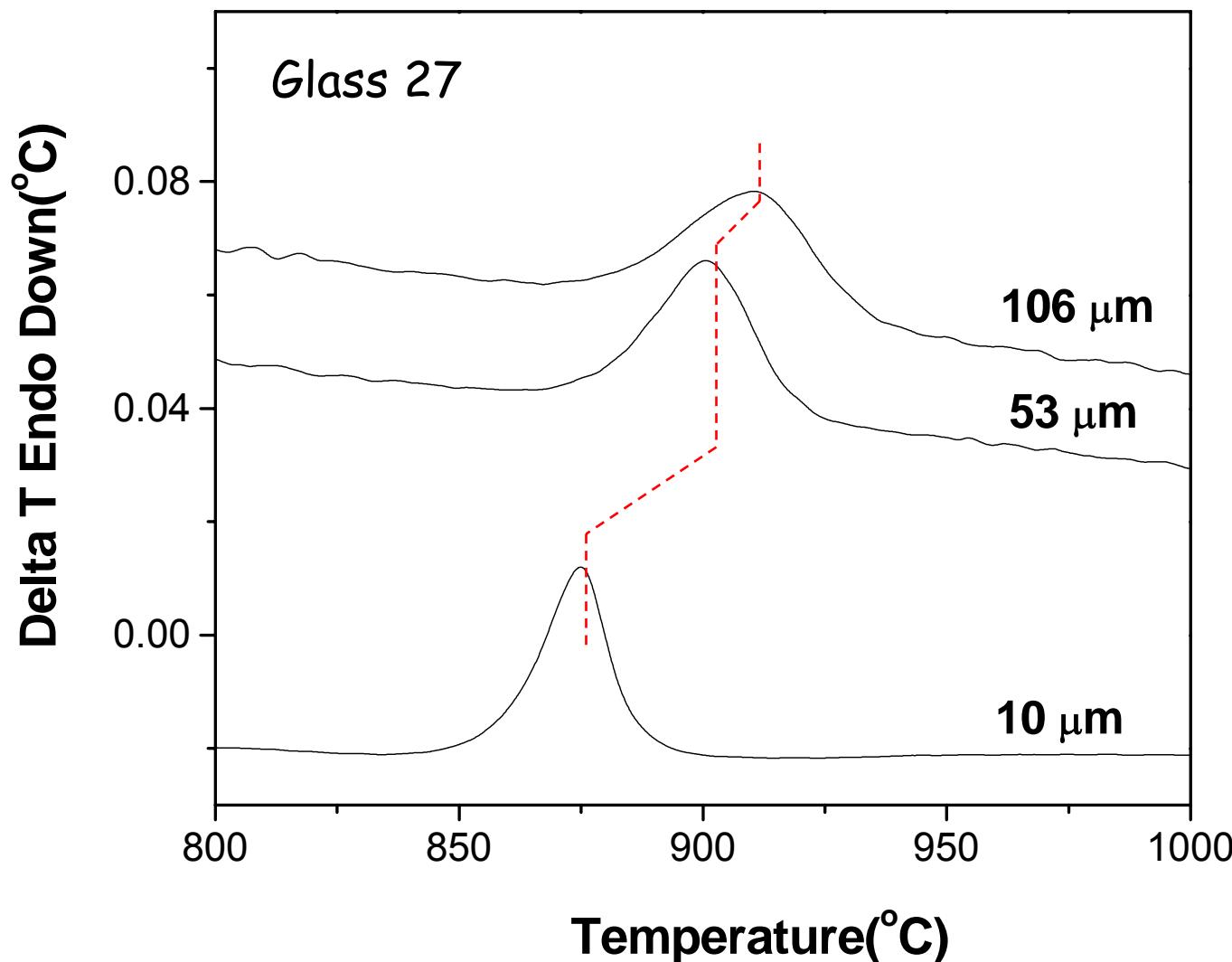
x is 'fraction crystallized', from DTA peak areas, ($x = A_0/A$)



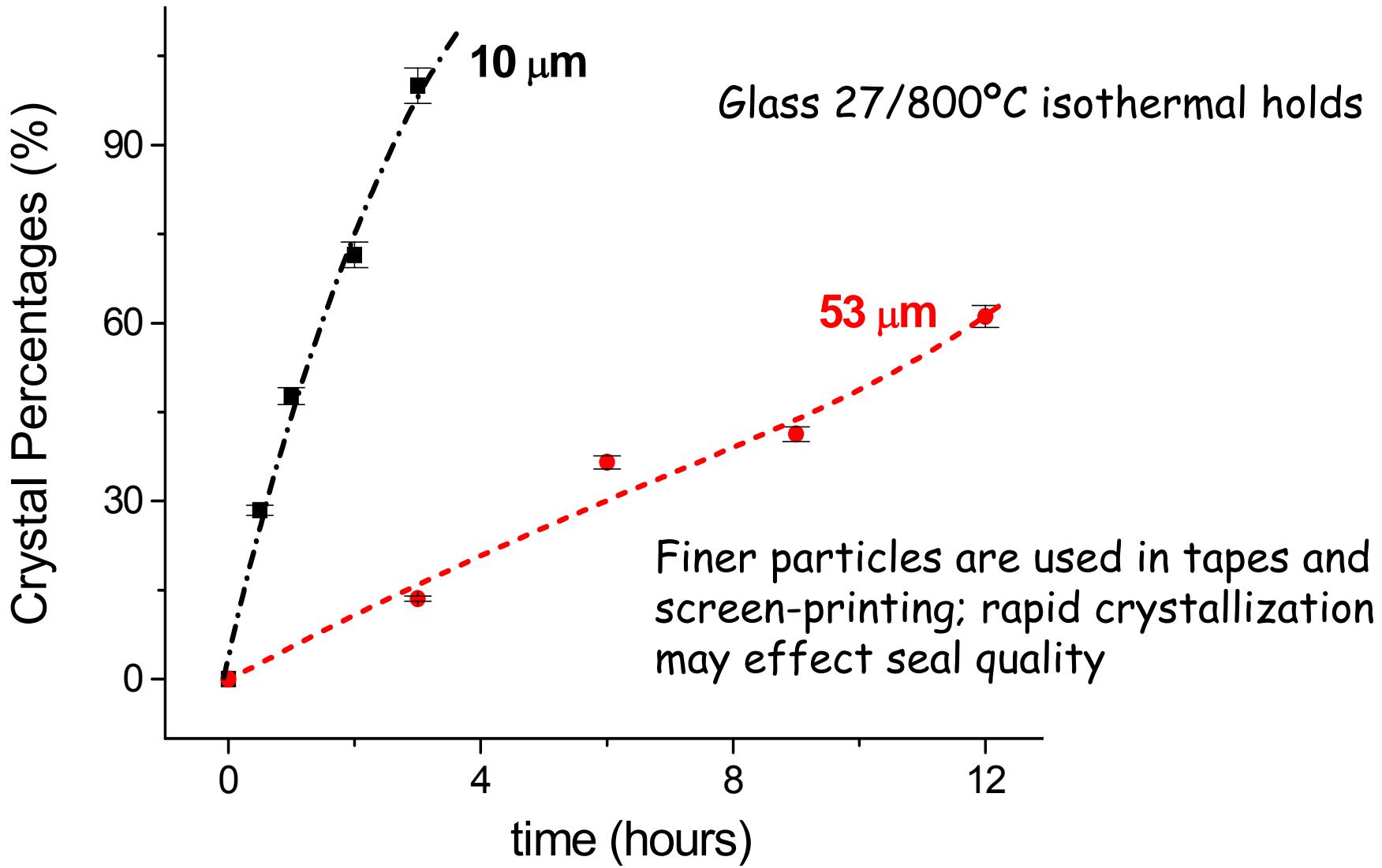
We have used this analysis to study:

1. Effects of particle size;
2. Additions of second phases

Crystallization temperature decreases with finer particle sizes



Crystallization kinetics are enhanced for finer particle sizes



Sealing materials can be modified by adding fillers

- Tailor CTE
- Control crystallization
- Affect interfacial reactions
- Relieve thermal stresses
 - Controlled cracking in glass matrix; healing by viscous flow of residual glass
 - Design CTE and elastic mismatches

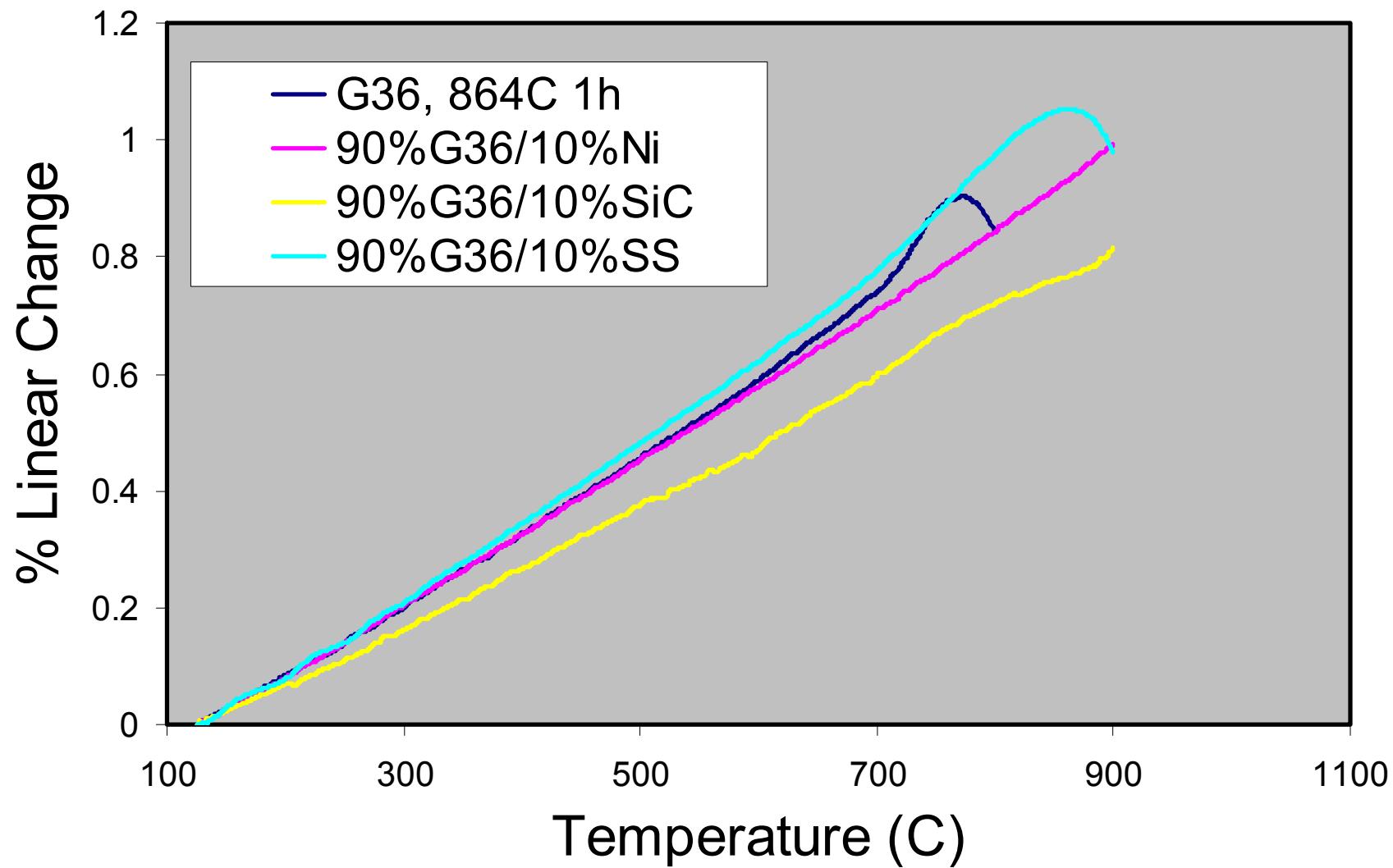
Composite Overview

Material	CTE (ppm/ $^{\circ}$ C)	Elastic Modulus (GPa)	Notes
G36	12.1	80	
Ni	13.3	207	
Mo	5.1	324	
316SS	17	193	
Ti-Ni		34-83	Phase transition
WC	5.2	669	
SiC	4.3	483	
Quartz	7.0→13.3		Phase transition
ZrO ₂	7.0→10.5	138-210	Phase transition

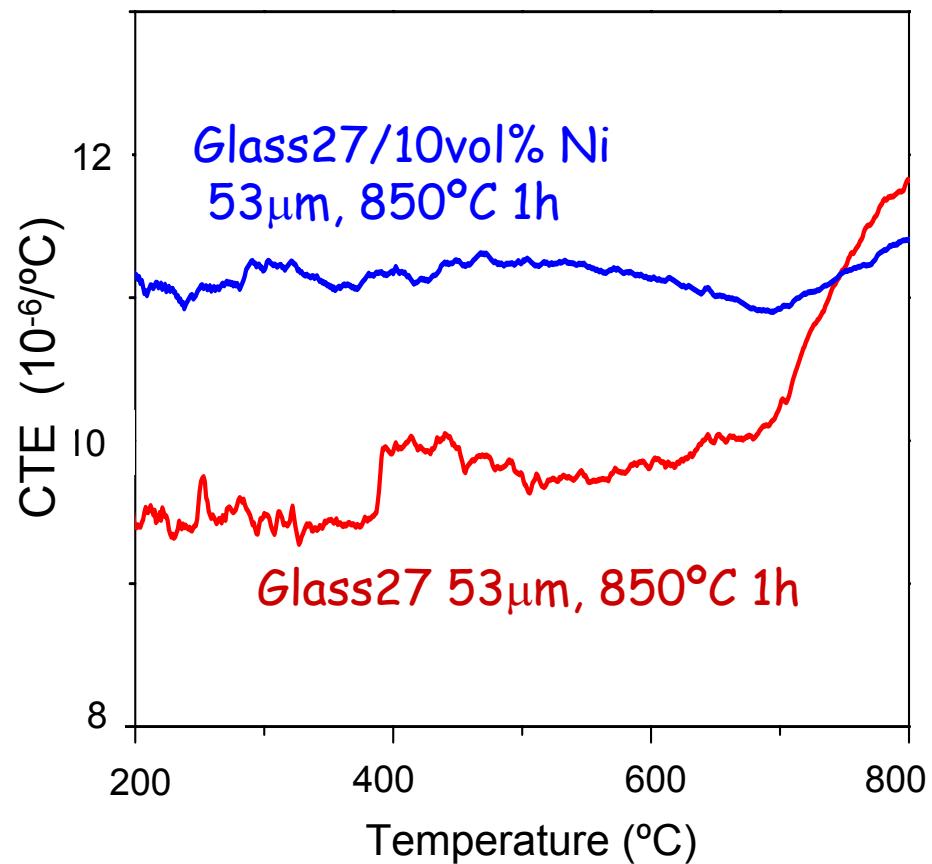
Composite Microstructure



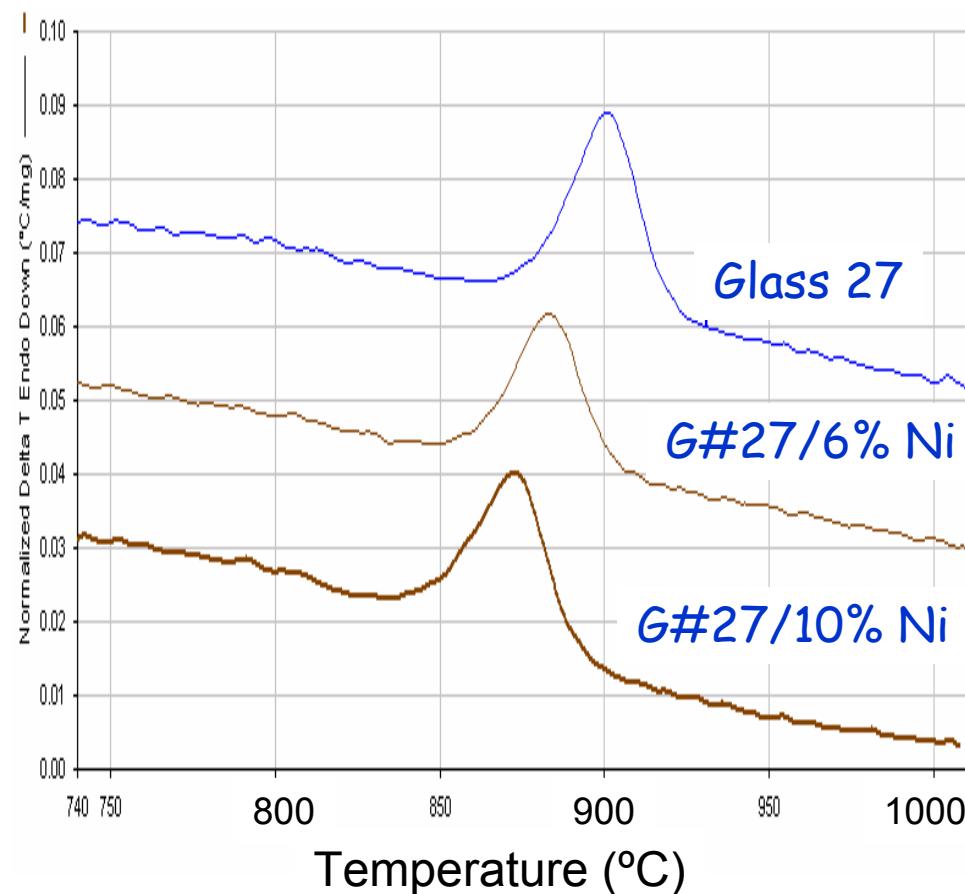
Dilatometric characteristics depend on filler



We are characterizing glass-filled composite sealing materials

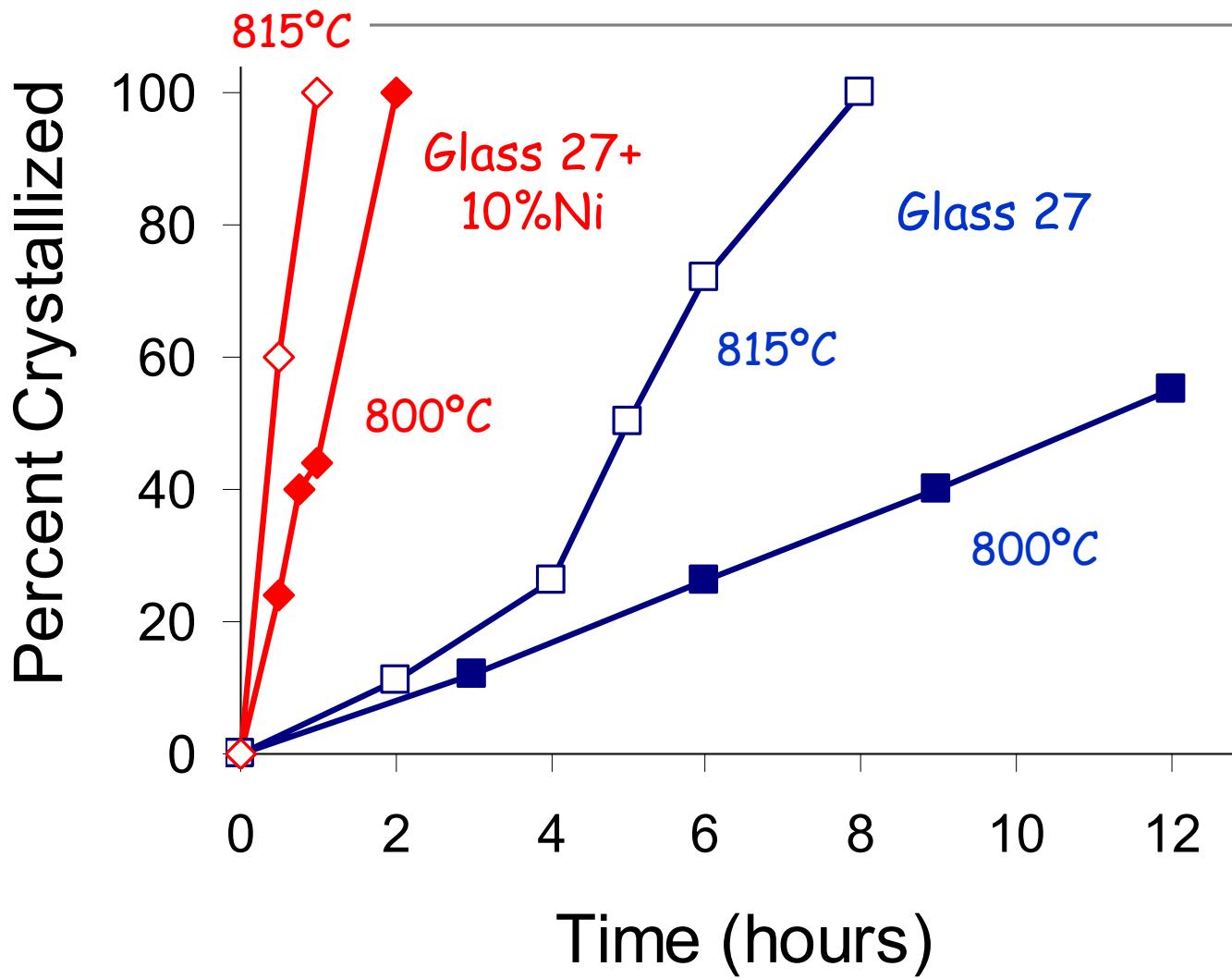


The CTE of a glass 27 composite increases with Ni content.

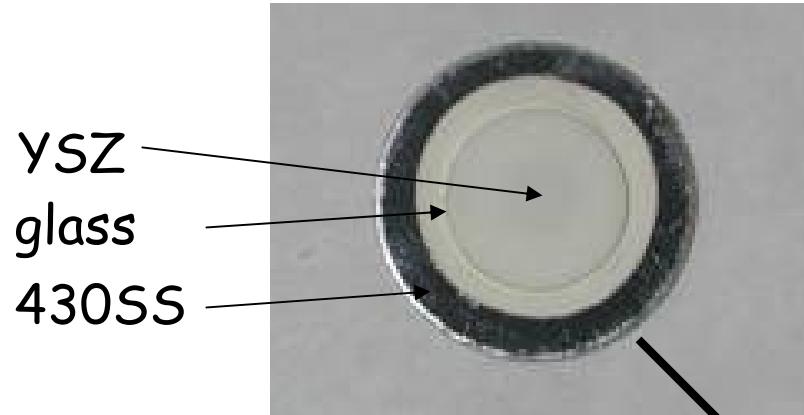
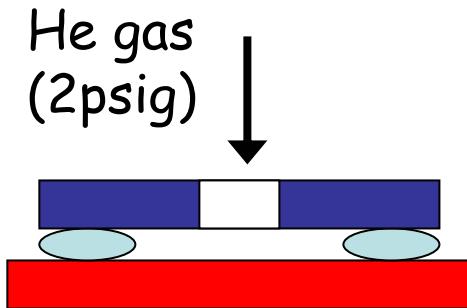


Ni reduces the crystallization temperature of glass 27

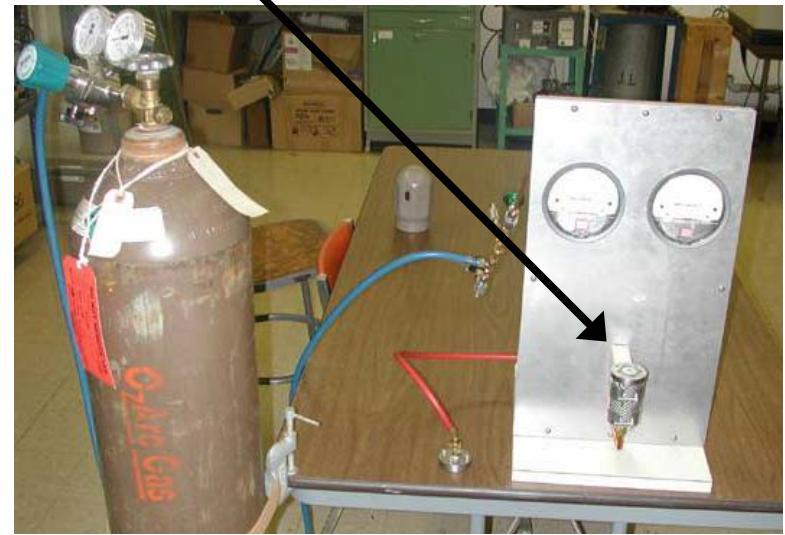
Ni additions enhance crystallization kinetics



Seal performance is being evaluated



- Glass tapes, 200 μm thick (PVB binder, 10 μm glass particles)
- Binder burn-out at 450°C (air)
- Sealed at 850-900°C (1-2 hours)
- Thermal cycle from 800°C
 - Hold 24 hours (forming gas or air)
 - -2°C/min to room temperature
 - Test for He-leak (2 hour pressure hold)



Seal performance is being evaluated

Tests in progress:

430SS/glass 50/YSZ

- 800°C/24 hrs/forming gas
- Seven cycles to room temp. (continues)

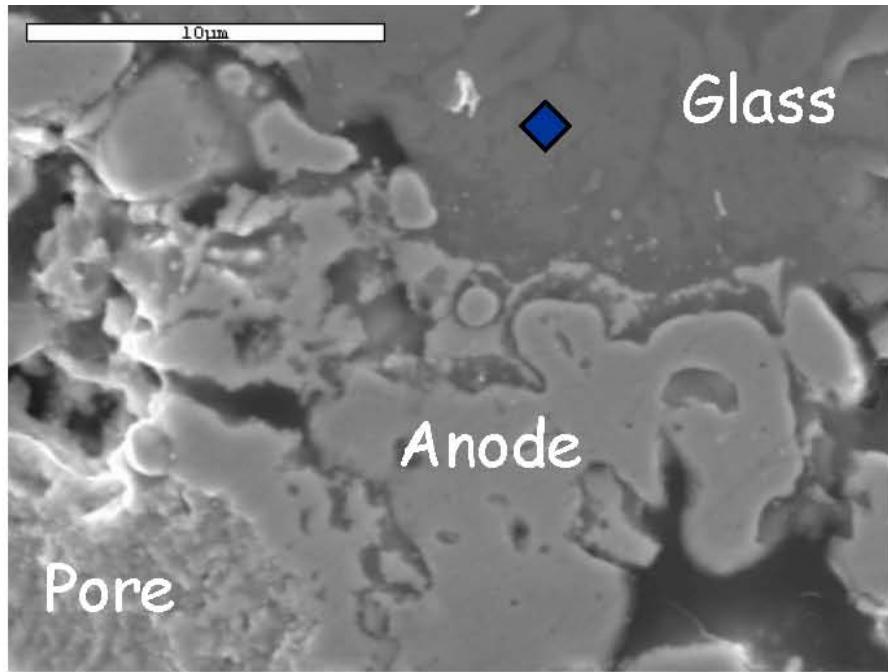
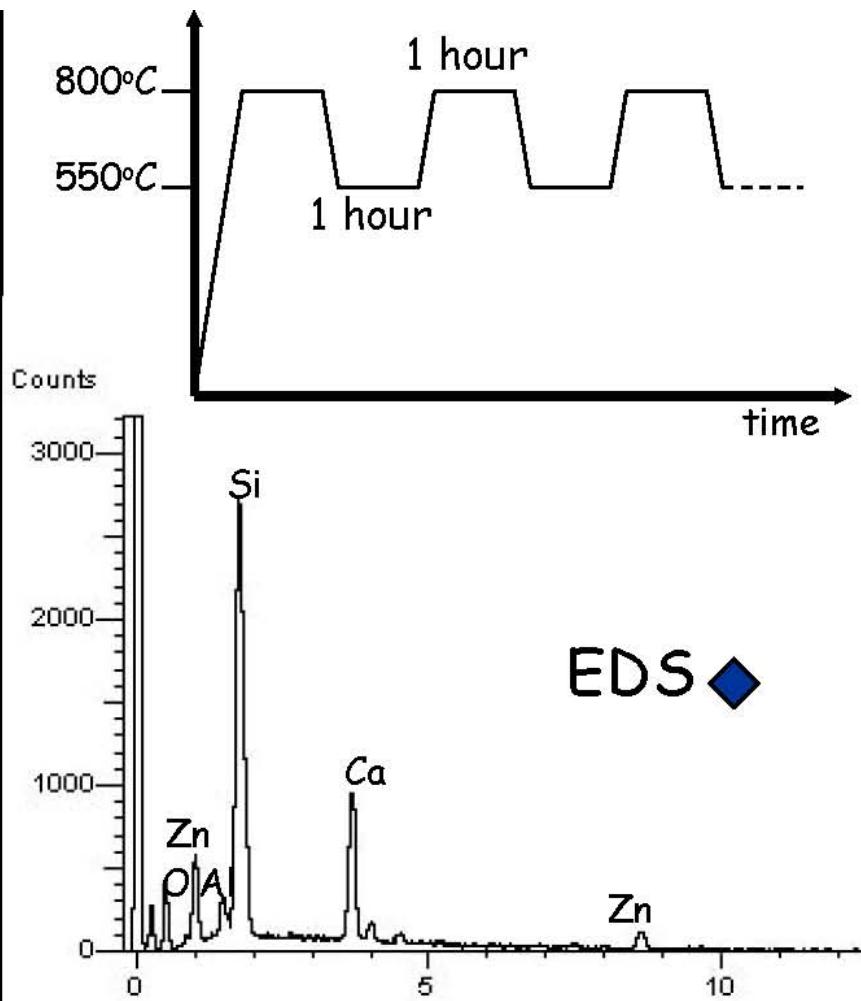


430SS/glass 50/Ni-YSZ anode

- 800°C/12 hrs/air gas
- Four cycles to room temp. (continues)



The glasses do not appear to react with anode materials



G#27/Anode interface after 11 cycles in Ar/H₂ atmosphere
(Ron Loehman, Sandia)

Experiments Underway

- Glass & composite processing
 - Dense seals using tape-casting techniques
 - Screen-printing techniques
- Hermetic prototype seals
 - 25 mm cells (anode/electrolyte/interconnects)
 - 100 mm cells
 - Hermeticity tests 'at temperature'
 - Thermal cycling tests
- Glass reactivity
 - Filler/matrix compatibility
 - SOFC interfaces

SOFC Seal Summary

- SOFC seals offer an interesting materials challenge
- RO- polysilicate compositions have promising combinations of properties
 - Polysilicate glass-ceramics can be designed with thermal and chemical properties desired for some SOFC seal designs.
 - Thermo-chemical and thermo-mechanical stabilities are critical for long-term applications.
- Composite seals based on RO-polysilicate glasses
 - Reduce stresses due to thermal cycling?

Thank you for your attention!